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Temporal and Spatial Patterns of Water Isotope Ratios (δ^2H and $\delta^{18}O$) in Municipal Tap Water as Measured by TCEA-IRMS

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14. ABSTRACT

An assessment of the spatial and temporal variability in water stable isotope ratios (δ^2H and δ^{18}O) was conducted during Spring–Summer 2011. Samples were collected from 12 locations within a single office/laboratory building over the course of three months to determine patterns in daily, long-term, and spatial variation. Samples were analyzed by quantitative high-temperature conversion elemental analysis (TC/EA), chromatographic separation, and stable isotope ratio analysis. The study revealed minimal daily variation and covariance in δ^2H and δ^{18}O. Seasonal variation was observed and was expected based on predictable variation in stable isotope ratios of environmental source water. Both δ^2H and δ^{18}O demonstrated an observable shift towards isotopic enrichment as the sampling period transitioned from Spring to Summer. This shift was concomitant with an increase in water temperature, volume, and conductivity of the source water. This investigation reveals that with consideration of predictable seasonal patterns in δ^2O and δ^{18}O, water stable isotope ratios provide a robust indicator of water sources.

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SUMMARY

An understanding of fine resolution variability in water stable isotope ratios is needed to ascertain the utility of water stable isotope ratios for observational purposes and sensor applications. While others have demonstrated that intra-annual ranges of tap water isotope ratios are relatively small (~10% difference) and large geographic distances yield large variation in tap water isotope ratios (Bowen et al. 2007; Kennedy et al. 2011) further assessment of short term variability and fine geographic resolution is required.

Here we present a laboratory assessment of the spatial and temporal variability in water stable isotope ratios (δ^2H and $\delta^{18}O$). Samples were collected from 12 locations within a single office building over the course of three months to determine patterns in daily, long-term and spatial variation. Samples were analyzed by quantitative high temperature conversion elemental analysis (TC/EA), chromatographic separation and stable isotope ratio analysis.

The study revealed minimal daily variation and covariance in δ^2H and $\delta^{18}O$. Covariance in δ^2H and $\delta^{18}O$ has been demonstrated by others (Bowen et al. 2007). Evidence of seasonal variation was observed and was expected based on previous reports (Kennedy et al. 2011). Specifically, both δ^2H and $\delta^{18}O$ demonstrated an observable shift towards isotopic enrichment as the sampling period transitioned from spring to summer.

This investigation reveals that with consideration of predictable seasonal patterns in δ^2H and $\delta^{18}O$ these analyses, and relative to global geospatial variations (Povinec et al., 2011), the methods used here provide a robust indicator of water sources.

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MATERIALS and METHODS

Sample Collection and Handling

A total of 94 tap water samples were obtained in triplicate from the Chemistry Building located at the Naval Research Laboratory in Washington. The sampling period spanned June through August, 2011. Water samples were collected in 15 ml glass vials with conical urea caps which were used to minimize headspace in the vials during storage. Taps were run for 30 seconds prior to sampling, and vials were triple rinsed with sample water before collection. Samples were stored inverted at 4°C while awaiting analysis. Samples were obtained from 12 rooms located on three floors in the Chemistry Building. The sampling design included taps that had fixed filtration units as well as water chillers in order to determine the impact that such water treatment would have on the reproducibility of the results.

For daily variation estimates, samples were collected from two separate taps every hour for 9 hours. For long term variation, samples were collected from the same two taps on a weekly basis spanning a period from June 1 to August 11, 2011. For the spatial analysis, samples were collected from 12 taps on a weekly to monthly basis during the entire sampling period (above).

TC/EA Analysis

Direct analysis of $^{18}O/^{16}O$ and D/H in liquid samples was carried out on a ThermoFinnigan High Temperature Conversion Elemental Analyzer (TC/EA). An auto sampler was used to inject an aliquot of water into a helium stream towards a high temperature glassy carbon reactor. At 1400 °C oxygen present in water was converted to CO, and hydrogen was converted to H_2 by pyrolysis. Reacted gases were transferred to a GC column and were separated isothermally at 75°C for individual analysis. Separated gases were then transferred to a ThermoFinnigan Delta V Plus Isotope Ratio Mass Spectrometer (IRMS) for analysis of stable

isotope ratios δ^2H and $\delta^{18}O$. A calibration curve of IAEA standards (VSMOW2, SLAP2, and GISP) for δ^2H and $\delta^{18}O$ values was used to generate a normalization equation which was applied to sample data. Data are expressed in the standard δ-notation as ‰, and are referenced to the VSMOW/SLAP scale.

RESULTS and DISCUSSION

Stable isotope ratios observed span a small range of values, from - 38.6 to -52.1‰ (±3.0‰) for δ^2H and -4.5 to -7.5‰ (±0.7 ‰) for $\delta^{18}O$. Strong co-variation between δ^2H and $\delta^{18}O$ was observed (Figure 1) with a general shift towards isotopic enrichment as the study progressed. Co-variation between δ^2H and $\delta^{18}O$ in drinking water supply has been reported by others (Bowen et al. 2007; Kennedy et al. 2011).

Minimal hourly variation in either δ^2H or $\delta^{18}O$ was observed (Figures 2A and 2B). For $\delta^{18}O$ the daily range was <0.2‰ and for δ^2H the daily range was <1‰. The values observed are within the precision range for sampling and analysis as estimated by experimental replicates.

The long term aspect of the study which included weekly and biweekly sampling of two taps indicate that there is an apparent seasonal shift in δ^2H and $\delta^{18}O$ during the course of the study. In late June, 2011, a shift towards isotopic enrichment was observed (Figure 3) which persisted towards the end of the study. Review of USGS gauge data for the Potomac River, the source of drinking water for the building in this study, indicates that this isotopic shift occurs concomitant with a mid season peak followed by rapid decline in river flow (Figure 4A), a moderate increase in water temperature (B) and a slight decrease in specific conductance (C). Without stable isotope ratio data on source water we cannot conclusively state that the apparent seasonal shift is reflective of the source water. However, based on the available USGS data, and the covariance between river flow, temperature and conductivity, we suggest that the features

observed are consistent with observations made by others where the seasonal change in precipitation rates imparts an isotopic "signature" on drinking water (Bowen et al., 2007).

The final aspect of this work was to ascertain fine scale geospatial variation in δ^2H and $\delta^{18}O$ within the building. Over the course of the study, stable isotope ratios in 12 locations generally co-varied (Figure 5) with the exception of one outlier. During June 2011, Tap 12 was significantly isotopically depleted (δ^2H and $\delta^{18}O$) with respect to other locations. The tap in question, a drinking water fountain, is physically situated in an under occupied section of the building. While we do not have an explanation for why the location exhibited patterns not observed elsewhere, the setting of the tap suggest that it was not flushed as frequently as other taps in more populated parts of the building. Thus, it is possible that stagnation of water in the supply lines, and recirculation in the chiller at this one location may have impacted the values observed. There is no indication that filtration or chilling specifically had any impact on this observation as three other filtered and chilled water taps were included in this work.

CONCLUSIONS

This study indicates that daily variation in δ^2H and $\delta^{18}O$ is minimal, and medium and long term variation at fixed locations is related to predictable patterns in local precipitation, and quality (temperature and conductivity) of source water. With the exception of one outlier, there is no fine scale variation in δ^2H and $\delta^{18}O$ within building, and water filtration and temperature control do not impact δ^2H and $\delta^{18}O$ values. Subsequent program plans need to be organized to compare sample data with other participants or expand the scope of the fine resolution study.

ACKNOWLEDGMENTS

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FIGURES

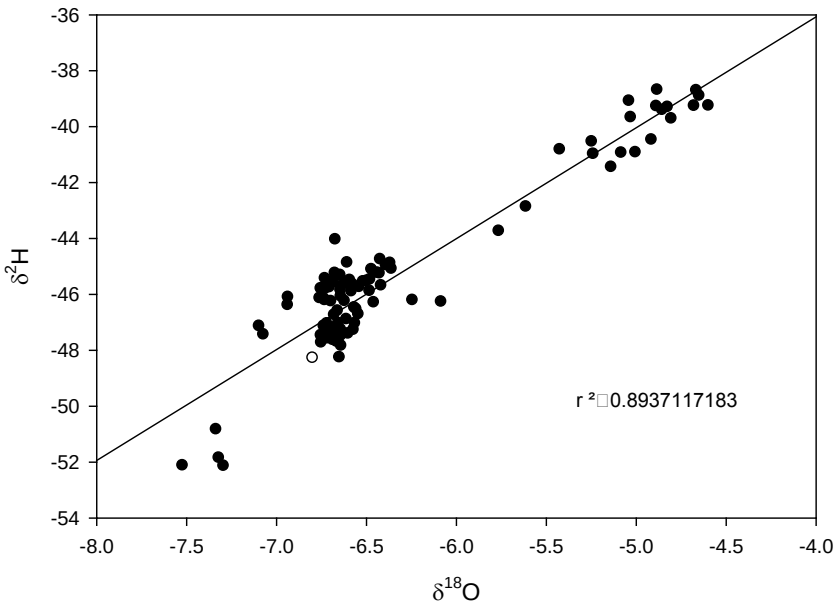

Figure 1. Single component linear regression of $\delta^{18}O$ plotted against $\delta^{2}H$. Regression statistics are reported. Measured values are reported in ‰.

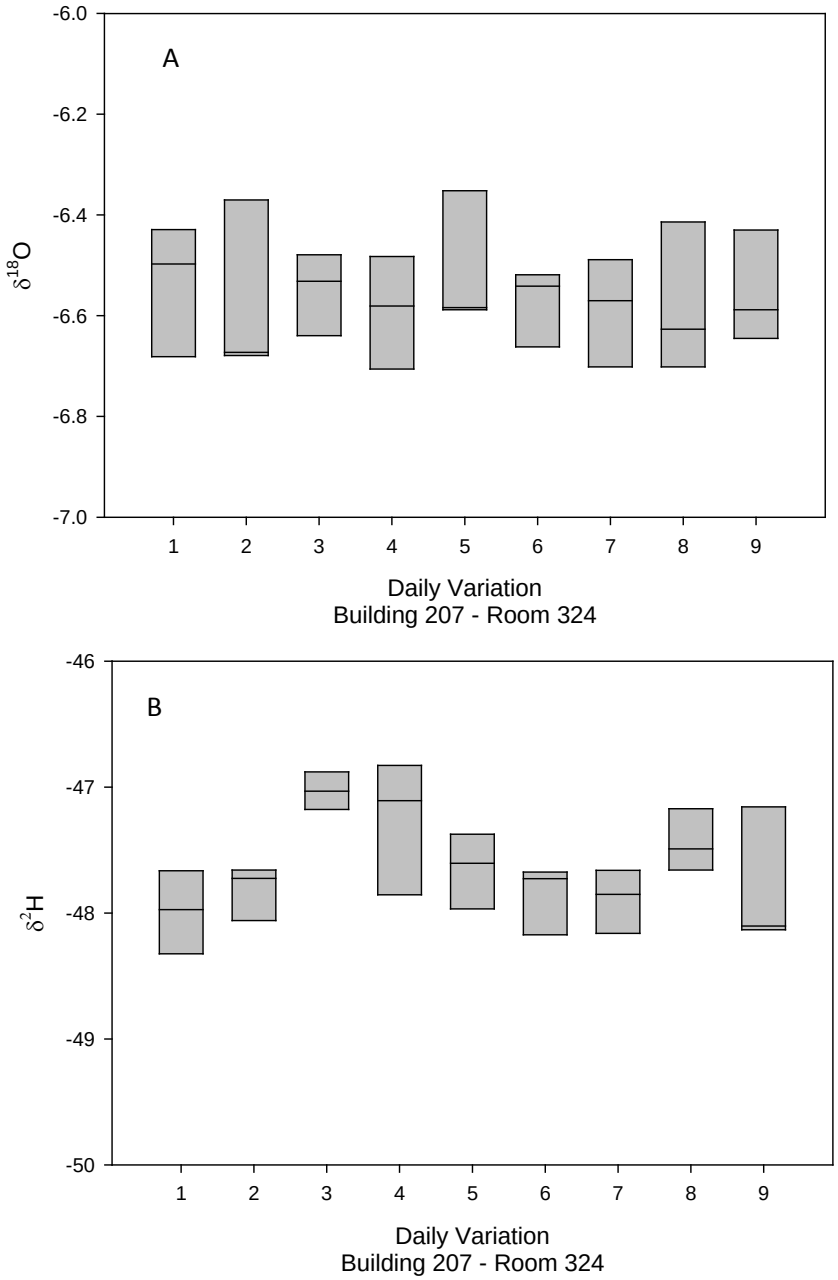

Figure 2. Daily variation in $\delta^{18}O$ (A) and $\delta^{2}H$ (B) in water samples collected at 1 hour intervals during a 9 hour period from a single location. Measured values are reported in ‰.

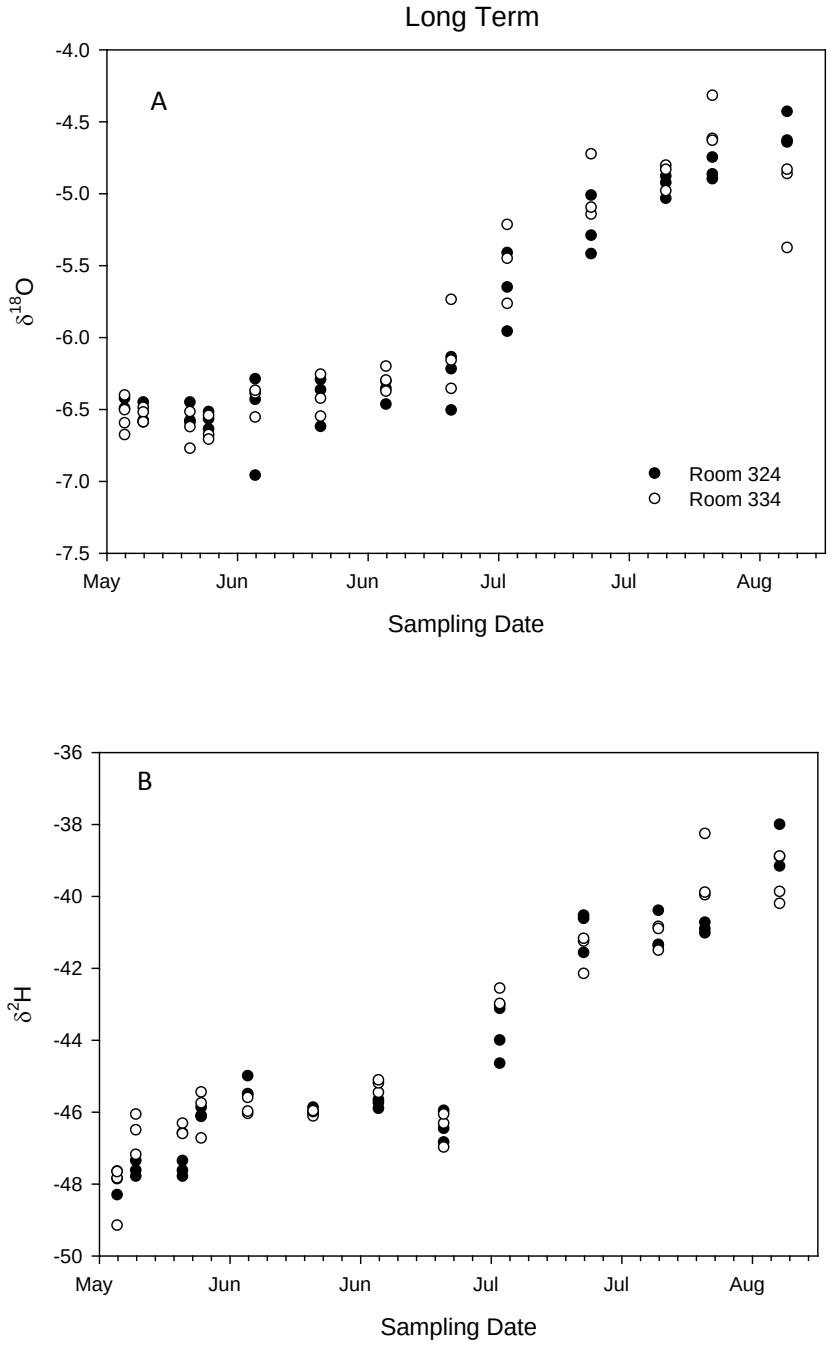

Figure 3. Long term variation in $\delta^{18}O$ (A) and $\delta^{2}H$ (B) in water samples collected weekly-bi-weekly during the three month study period from two separate locations. Measured values are reported in ‰.

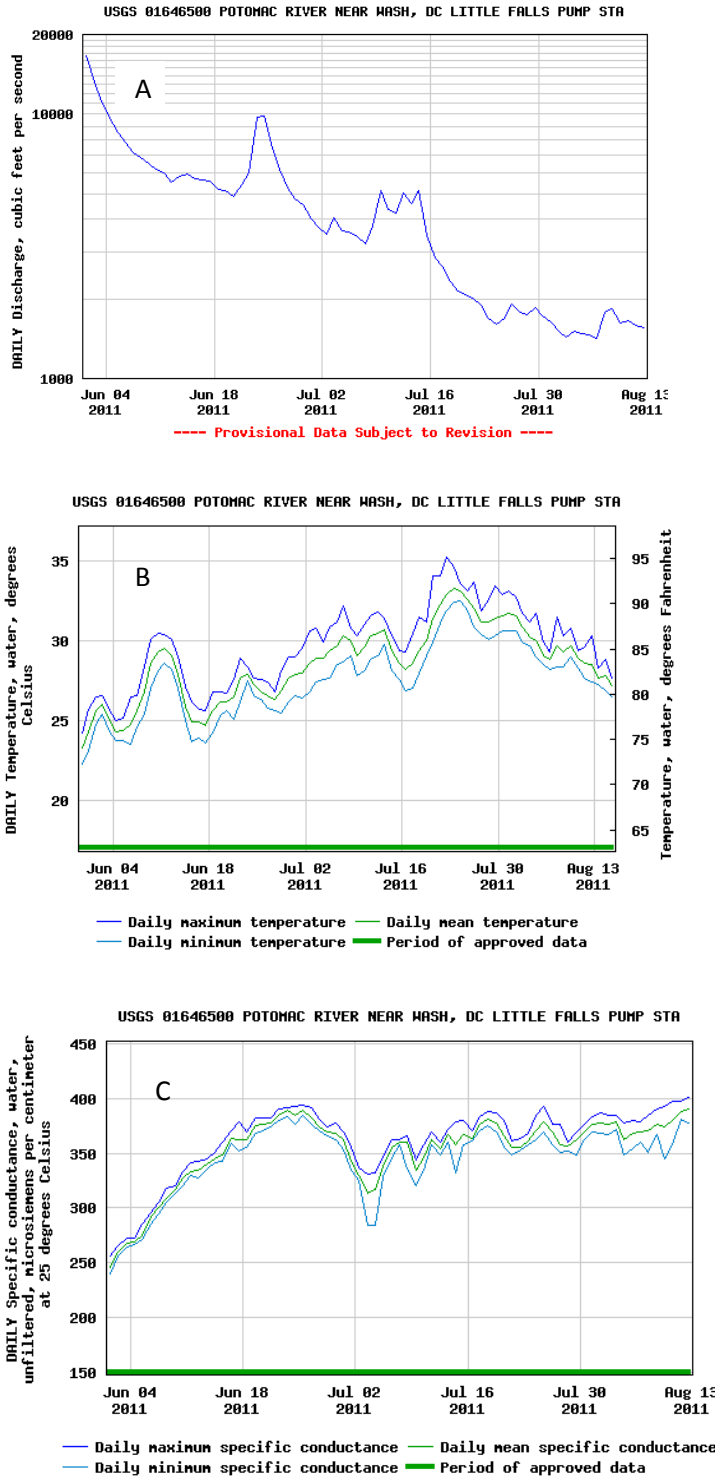

Figure 4. USGS river flow gauge data from Little Falls Pump station located on the Potomac River approximately 4 miles north of the study location. Reported data are for daily discharge (A), daily temperature (B) and specific conductance (C). Source: www.waterdata.usgs.gov.

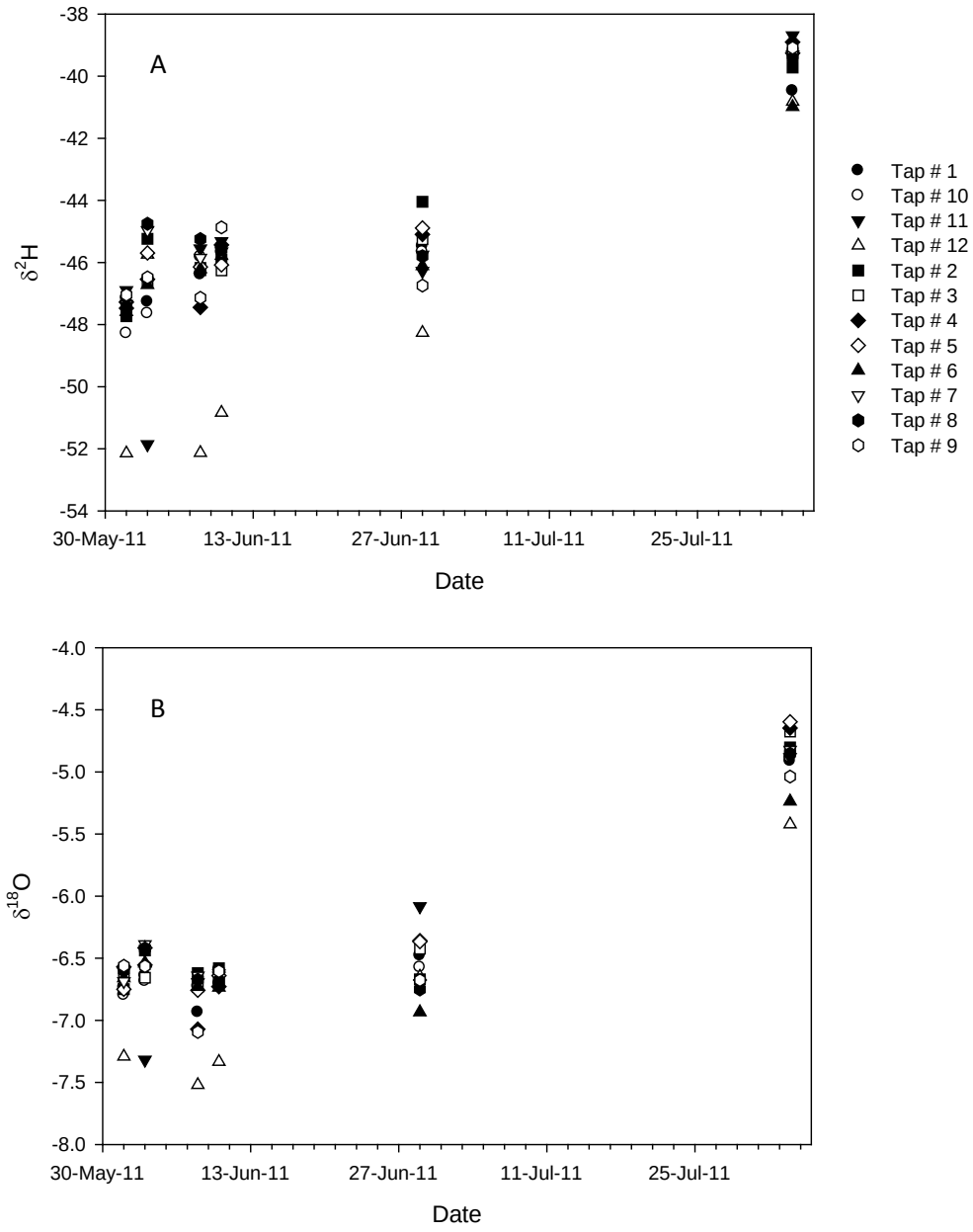

Figure 5. Spatial variation in $\delta^{18}O$ (A) and $\delta^{2}H$ (B) in water samples collected weekly, bi-weekly and monthly from 12 locations during the three month study period. Measured values are reported in ‰.